

# Nano graphite produced by rapid grinding as an anode for lithium-ion batteries

## Abstract

Reducing the particle size of active materials is an effective solution to the performance degradation of lithium-ion batteries. In this study, we proposed a simple strategy for preparing Nano graphite as the anode of lithium-ion batteries by the rapid mechanical grinding method. Diamond particles have been selected as the medium for the first time to achieve high processing efficiency and low energy consumption. The 10-300 nm Nano graphite produced in this way exhibits an intact structure and a high specific surface area. The introduced oxygen atom increased the wettability of the Nano graphite electrode and reduced its polarization. Nano graphite produced after 3 hours of grinding shows an excellent reversible capacity of 191 mAh g<sup>-1</sup> at a rate of 5 C after 480 cycles, with an 86% increase in capacity at 1 C compared to pure graphite[1,2]. The culmination of this strategy is the optimization of current manufacturing methods. Excellent electrochemical performance results from the combined effect of Nano scale particle size, large specific surface area, and continuous mesopores. Foreword ion battery (LIB), which is one of the indispensable energy storage devices in the world of production and daily life, has various merits such as high average output voltage and high energy density. Environmentally friendly. Li + intercalation / DE intercalation plays an important role in the storage and release of electrical energy converted from the chemical energy stored in the compound, forming a solid engineering foundation for LIB. LIB performance assessments are based on several key indicators such as charge and discharge capacity, lifespan, and rate performance. Graphite is considered to be the most ideal anode material in LIB and is widely used in commercial applications due to its stable electrochemical performance and high theoretical specific volume (~ 372 mAh g<sup>-1</sup>). However, the inadequate fast charging capabilities of graphite-based LIBs have hampered further development of LIBs, especially in electric vehicles and power grid applications. In recent years,[3,4] few studies have focused on Nano scaling from graphite to Nano graphite. This is mainly due to the fact that delamination along the plane of the layered material overcomes the van der Waals forces. Along the direction perpendicular to the plane of the layered material, the cooperation between the atoms in the plane of the layered material must be cut off. For example, the shear force applied vertically to graphite is 28 times the van der Waals force overcome in the planar direction. Nano graphite usually provides more effective space and active sites for lithium ion storage and facilitates the movement of lithium ions during charging / discharging. Conventional mineral processing methods for producing Nano graphite have been established, including ball mill milling and mechanical milling. In this method, graphite is tapped from top to bottom to grind and refine the bulk material to Nano size.

## Materials and Methods

### Fabrication of Nano-Graphite

Nano-graphite was prepared from natural flake graphite (1200 mesh, Shanghai Macklin

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Biochemical Co., Ltd., Shanghai, China) by using a rapid pulverization method with the introduction of diamond particles (80 meshes, Ai-zuan Novel Materials Co., Ltd., Shangqiu, China). The mass ratio between natural flake graphite and diamond particle was the grinding speed was set to 2800 rpm, and the grinding time varied from one hour to three hours. The as-pulverized Nano-graphite materials were dispersed into isopropanol solution concentration of 10 mg mL<sup>-1</sup>. After that, the dispersion was centrifuged at 3000 rpm for 10 min, and the supernatant was taken to obtain high-quality Nano-graphite dispersion with an average particle size of 300 nm [5,6]. The Nano-graphite materials prepared according to different grinding times were named as NG-x, where NG stands for Nano-graphite, and x represents the grinding time

#### Structural Characterization

The prepared Nano-graphite samples are systematically characterized by various measurements, including UV-visible spectroscopy powder X-ray diffract meter Raman spectrometer Renishaw In Via, Gloucestershire X-ray photoelectron spectroscopy Versa Probe Waltham, zeta potential and granular meter (Anton Paar, Litesizer™ 500, Shanghai, China) scanning electron microscopy (SEM, Hitachi SU8010, Tokyo, Japan) surface area and pore size analyser (Anton Paar, Nova touch Quanta chrome, Shanghai, China) and galvanostatic charge/discharge measurement. The lithium-ion semi-battery measurements were carried out by using a half-cell system in CR2032-type coin cells. Nano graphite was mixed with Super P and polyvinylidene fluoride binder to form slurry with a weight ratio of Electrodes were prepared by casting the slurry onto copper foil using a doctor blade and drying in a vacuum drying oven at 60 °C [7,8]. for 6 hours. The load level of the active substance is about 0.8 mgcm<sup>-2</sup>. The electrodes were cut into a circle with a diameter of 12 mm for the coin battery test. Lithium-ion batteries are assembled using lithium as the counter electrode. The electrolyte was 1.0 M LiPF<sub>6</sub> in ethylene carbonate / diethyl carbonate the volume ratio was and polypropylene (PP) membrane was selected as the separator. The coin cell batteries are manufactured in an AR atmosphere (H<sub>2</sub>O and O<sub>2</sub> <0.01 ppm) glove box. The lithium-ion battery was cycled

between 0.01 and 3V at a constant current density of 0.1 C in a 25 °C LAND CT2001A battery test system. Various currents in the range of 0.1-5 °C were also used to measure the electrochemical reaction [9,10].

## Results and discussion

Currently various methods for producing nanoparticles, such as mechanical grinding and ball milling, have been established. Here we report a new rapid grinding method for preparing nanoparticles in this study (Scheme). The rapid exfoliation here is based on the shear forces provided by the diamond perpendicular to the plane of the layered graphite flakes. The rotating crushing hammer in the cavity creates a strong wind field that moves the mixture in order at high speeds of 2000 rpm. Due to the synergistic effect of centrifugal force and gravity, the grinding hammer collides and generates a strong impact force perpendicular to the graphite surface. Graphite flakes are crushed at the collision surface as they collide with diamond particles. Shearing is applied in the plane direction of the graphite flakes to reduce the particle size [11,12]. Due to the small size of the diamond particles, the particle size of the product obtained after the addition of diamond is significantly reduced in the same grinding time compared to the case without the addition. Represents the surface area and pore size distribution based on the BET theory. According to the nitrogen adsorption / desorption curve, the Bruner-Emmett-Teller (BET) specific surface area of is significantly increased. Compared with pure graphite. The specific surface area of NG-3 is smaller than the theoretical value of mesoporous materials, but this value (138 is the same as the previously reported value of grapheme Nano sheets. The same is true g-1). In addition, as shown in Figure 4a, both the NG-3 and pure graphite curves show a typical IV type isotherm adsorption curve and a hysteresis loop consistent with the H3 classification, forming numerous mesoporous channels. Shows material accumulation. . The pore size distribution map in Figure 4b shows that the average pore radius is about 2.2 nm for NG-3 and 1.8 nm for pure graphite, based on the BJH model. This further proves the presence of mesoporous in NG-3. The increased pore radius of NG-3 and the non-uniform distribution of chaotic

mesoporous are mainly due to the random directional shear forces and the non-uniform distribution of the defects generated during the grinding process [13,14]. In addition, the microspore volume is only 0.05 cm<sup>3</sup> g<sup>-1</sup>, indicating very low microspore content. To characterize the resulting Nano graphite, three different Nano graphite materials from different mills named, and were dispersed in an isopropanol (IPA) solvent and subjected to a centrifugation process. Separated. And it was redistributed into IPA. The stability of the Nano graphite dispersion under centrifugation at 3000 rpm was checked after standing overnight. Quantitative analysis of concentration differences was performed using UV-Vis absorption spectra. The intensity of the curve in the 400-800 nm range is times the intensity of the other curves, which means that the concentration of is also times higher[15].

## Conclusion

A simple process has been devised to produce Nano graphite using diamond-based grinding techniques that mix diamond with natural graphite and cut it into Nano sizes with the power of a crusher paddle. The particle size of the Nano graphite produced in this way ranges from 10 to 300 nm, and the specific surface area is as high as 138 m<sup>2</sup> g<sup>-1</sup>. Nano-sized graphite increases the contact area between the electrolyte and the electrode material and shortens the Li + diffusion path within the graphite. As a result, capacitance increases with increasing current density. NG-3 shows an excellent reversible capacitance of 191 mAh g<sup>-1</sup> at a high current rate of 5 C in LIB, much higher than natural graphite. Compared to traditional Nano graphite manufacturing methods, which are costly, current methods, not only allow large-scale, low-cost manufacturing, but also achieve high manufacturing efficiency and low energy consumption. The scalable method developed in this study should enable Nano graphite to become a potential anode material for next-generation high-speed LIBs.

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